U.S. ENVIRONMENTAL PROTECTION AGENCY
COMMENTS ON
BACKGROUND GEOCHEMICAL CHARACTERIZATION REPORT FOR 1989

GENERAL COMMENTS

1. The report includes some types of water quality analyses that are appropriate, i.e., stiff diagrams and trilinear diagrams. However, the report should be more comprehensive in terms of explaining the evolution of the groundwater quality. Since natural groundwater quality is in large part a function of the aquifer media through which it flows, the report should include a discussion of the mineralogy of the geologic units which are considered in the report. Background concentrations for naturally occurring analytes may vary depending on where in the flow system the sample is collected.

2. The report should include a better discussion of groundwater/surface water interaction. It is known that groundwater discharges from the Rocky Flats Alluvium, the valley fill alluvium, and possibly the colluvium within the Rocky Flats site. Groundwater discharging from these geologic units enters surface streams (Walnut Creek, Rock Creek, Woman Creek or their tributaries) as base flow or as overland flow (from seeps). Analyses of water quality data from wells and surface water stations should attempt to quantify the contribution to surface water from groundwater discharge.

3. EPA suggests that future reports contain summary tables which include the maximum, minimum, and mean concentration values and standard deviations for each analyte in each analyte group for each medium. The way the data is presented in the report makes it difficult to determine the range of concentration values for a given analyte for a given medium. The groundwater data and the borehole data should be summarized by geologic unit.

4. While the statistical and probability estimation methods that were applied to the data were useful for determining differences in variances and non-detects between subsets of data, EPA has concerns about computing only one set of tolerance intervals and summary statistics for surface water (except for Ca, Li, and Na) and sediment samples. Considering that temporal effects have not been analyzed, it may be incorrect to treat all surface water quality data as one set of data. Initially, the sediment samples from the headwaters of Rock Creek, Walnut Creek, and Woman Creek should be treated separately when computing tolerance intervals and summary statistics. This is especially true if a mineralogical analysis indicates significant differences between the sediments deposited by the three creeks. Only after sufficient data has been collected can it be determined if it is appropriate to combine the analytical data for each drainage into one database for statistical comparisons.

Exh. 1

5. EPA suggests that the borehole and groundwater samples from weathered claystone, weathered sandstone, and unweathered sandstone be identified as to whether they are from the Laramie Formation or the Arapahoe Formation. This is important since the Arapahoe Formation is a major bedrock aquifer in the Denver area.

SPECIFIC COMMENTS

1. Figure 2-1:

a. The figure is confusing because the test for outliers is indicated as occurring after data has been rejected. However, the text indicates that the test for outliers is meant to identify data which should be rejected. It appears that the "test for outliers" box needs to be moved to the location before the "treat rejected data as missing values" box. Also, why is >3 detects a decision point? What is the statistical significance of 3 detects given the variation in the number of samples collected per medium?

b. The draft Background Hydrogeochemical Characterization and Monitoring Plan (Rockwell, 1989) indicates that Dixon's Test or Rosner's Test will be used to test for outliers. What is the rationale for using the ASTM methodology and deviating from the workplan? This needs to be indicated in the text.

2. Page 2-4, Section 2.4.1, Comparisons Between Groups:

a. If, as the report states, the spatial variable was envisioned as a comparison of analyte concentrations between the three drainage basins, why was only one background station sampled in the Walnut Creek drainage basin? This makes it difficult to do an adequate analysis of variance for surface water and stream sediment data. Does DOE intend to maintain this sampling schedule or to add more sampling stations to achieve the required spatial comparison? EPA suggests that more stations be added. The appropriate number of stations should be determined statistically. The draft Background Hydrogeochemical Characterization and Monitoring Plan (Rockwell, 1989) envisioned only one monitoring station for the Walnut Creek Drainage. EPA suggests that this be revised for future reports.

b. The division of the RFP into North and South Rocky Flats may not be appropriate for the lower groundwater flow system since it is probably not hydraulically connected to the surface creeks. Potentiometric surface maps and bedrock contour maps are required to verify the assumption that a groundwater divide exists within the lower groundwater flow system. Also, it is not appropriate to combine Walnut and Rock Creek drainages. Just as there is a groundwater divide for the upper flow system between Woman and Walnut Creeks, there is also a groundwater divide between Walnut and Rock Creeks.

c. The text states that ground water samples were classified by the geologic unit in which the well is screened. As stated, weathered bedrock was included in the surficial deposits. EPA assumes that the grouping was based on the hydraulic interconnection between the surficial deposits and the weathered bedrock however this is not explicitly stated in the text. Include an explanation. Additionally, an explanation of how the depth of weathered bedrock was determined is needed.

3. Page 2-8, last paragraph: If analytes do not have greater than 50% detectable concentrations, the detection limits of the analytes must be reviewed for adequacy.

4. Page 2-9, Section 2.4.2, Calculation of Tolerance Intervals: Tolerance intervals computed from a small data set are weak for use in comparing background to single sample analyte values.

5. Page 2-12, Section 2.4.3, Radiochemistry Statistics:

a. EPA assumes that the reference in this section to "blank subtraction" is the subtraction of instrument background from the gross counting result (instrument + sample). This is a standard procedure as indicated in this section. Therefore, EPA does not concur with the proposal to discontinue this practice. EPA recommends continuation of blank subtraction with the addition that negative values be reported as less than the MDA. A table of MDA values should be included. Also, please provide an explanation of why information is not available to un-correct the analyses of radiochemistry. Data from the analysis of blanks must be reported and reasonable estimates of the MDA's for the radiochemistry analyses must be reconstructed in order to interpret the results of this report.

In the case of the total tritium in surface water, please provide an explanation of why it is probably inappropriate to replace the blank subtracted value with the MDA.

b. It is important to state the means of radiochemical analysis for comparison of sample data. Provide an explanation of whether or not the samples were analyzed wet or dry. The moisture content of the samples should be reported if the samples were analyzed wet. Standard procedures normalize the results to dry weight.

c. Are tritium analyses for sediments indicative of the tritium concentrations in the overlying water column?

d. The high radium and gross alpha results for surface water station SW80 are not fully explained by the presence of suspended solids. Radium values are an order of magnitude higher than average for surface water values. The sample would have had to contained a very large amount of mud to account for the difference in which case it was likely not a surface water sample. Additionally, the gross alpha value is an order of magnitude greater than the values for plutonium, americium, radium and uranium together. The remaining alpha activity is not accounted for. This could possibly be due to the presence of a thorium source or most likely, poor analytical and sampling techniques. Resampling is required.

6. Page 2-13, Section 2.4.4, Seasonality: DOE states that at the present time, there is insufficient data available to establish tolerance intervals on a seasonal basis yet does not state the amount of data that is considered to be sufficient. Please indicate in the text how many quarters of sampling data is considered to be sufficient to determine seasonal variation. An approach to determining seasonality must be decided upon as soon as possible in order to implement any changes especially if monthly sampling is preferred over quarterly sampling over a three year period.

7. Page 2-13, Section 2.4.5, Comparison of Background and Non-Background Data: The extent by which the tolerance limit is exceeded will give some insight as to whether the cause of the exceedence is a chemical release. The evaluation of non-background and background data needs to include technical judgement as well as statistical analysis. However, judgmental determinations must be explicit and must occur after the statistical analysis.

8. Page 2-15, first paragraph: The discussion on natural geochemical evolution is valid for the naturally occurring radionuclides but is not valid for the man-made radionuclides.

9. Page 3-1:

a. How does the QA/QC Plan prepared by Rockwell International and used in the sampling and analysis for the background program differ from the Site Wide Quality Assurance Project Plan? The significant differences between the two plans must be analyzed and the appropriate changes must be made in the background program to allow the RFI/RI data to be correctly compared to background data. Additionally, will the background program now utilize the standard operating procedures developed for the RFI/RI program?

b. How was the lower boundary of the surficial groundwater flow system determined? This should be discussed in the text.

c. It is stated that the aquifer materials in the Rock Creek flow system are lithologically similar to those in the north and south Walnut Creek areas. What is meant by this? Does this statement also mean that the bedrock aquifer materials are similar in the two drainage basins?

d. Groundwater may also move through the surficial cover to bedrock via weathered bedrock as well as bedrock sandstones.

10. Figure 3-2: Drainages need to be labeled in Figure 3-2. The potentiometric surface depicted in Figure 3-2 is too detailed for the number of data points (well locations). It should be mentioned in the text, that the map was generated from assumptions and may not necessarily be accurate for the areas where control is lacking.

11. Page 3-5:

a. In determining if a well was dry as a result of the water level being below the screened interval, it is necessary to record depth to the bottom of the well and the bottom of the screened interval.

b. Ground water sampling rounds must be conducted in a shorter period of time if seasonality is to be adequately addressed and correlation of data is to be accurate. For example, round 1 sampling in 1989 extended from April to July. This period covers spring runoff and part of summer drying. Correlation between water level and measurements and seasonal effects for round 1 would not be possible with this schedule.

12. Page 3-7, section 3.2, Surface Water:

a. Three sampling stations identified as surface water monitoring locations (SW080, SW104, and SW108) are actually groundwater seeps. It is inappropriate to include water quality data from these seeps in the statistical analyses of surface water quality data. Inspection of the geology map indicates that these seeps may be discharging from the Rocky Flats Alluvium. Water quality data from these seeps should be included with other water quality data from the Rocky Flats alluvium not with surface water data.

b. Surface water monitoring station SW041 is downgradient from Rocky Flats Lake and according to the text, the station is affected by lake discharge and irrigation needs. An analysis of whether the surface water from the station is representative of background must be performed since the water is channeled through an irrigation canal.

13. Page 3-8, Section 3.4, Borehole Samples:

a. The text states that borehole B400189 was drilled in the southwestern buffer zone. It also states that Table 3-5 describes the samples collected from borehole B400189. However, borehole B400189 is not listed in Table 3-5. It may be that there is a typo in Table 3-5 and that B405189 should be B400189. Please check and correct as required.

b. Table 3-5 should specify if a split-spoon, split-tube sample, or cuttings were collected for each borehole. Also, Table 3-5 should indicate if the sample interval was in bedrock or surficial deposits.

c. Why were composite samples collected from the boreholes? The use of a split-spoon should allow for the collection of a discrete non-composited sample. By collecting composite samples, it is difficult to tell which lithologic unit is being analyzed.

14. Page 3-10, last paragraph: What is the rationale for excluding trivalent chromium from the borehole analyses? This form of chromium tends to be adsorbed strongly to soil components. This would seem to be rationale for including it in a chemical analysis.

15. Page 3-15, Table 3-2: The final note on this page regarding the decision tree requires clarification. Is this the total gross alpha concentration or the total gross alpha concentration minus the uranium concentration?

16. Page 4-1, Section 4.1, QA/QC Practices:

a. Why were the background samples not analyzed for organics?

b. The background analyses for radionuclides is inadequate. The use of rejected radionuclide data in statistical computations is unacceptable.

17. Page 4-2, first paragraph: In reality, the determination of areas of contamination should not be made on the basis of gross alpha and beta results. These determinations should be based on the specific radionuclide data. EPA suggests that a note be added to the text to reflect this.

18. Page 4-2, Section 4.2, Status of Data Validation:

a. Why has less than 3% of the radionuclide data been reviewed? Also, none of the dissolved radionuclide data have been validated. This severely limits the use of the data for background analyses. The use of rejected radionuclide data in statistical computations is questionable. The background analyses for radionuclides is inadequate.

b. Problems in the analytical techniques are apparent given the high percent of rejected data (i.e. the negative readings for metal blanks in ground water, surface water, and sediments, the low matrix spike recoveries for cyanide, the outdated self absorption curve for radionuclide data, low chemical recoveries, and incorrect sulfide data in sediments). In addition, all radionuclide data was not validated. The background report cannot be considered complete without evaluation of all the pertinent data. Problems with analytical techniques and data validation greatly impact data evaluation and background characterization.

c. The large error term for the radionuclide data indicates that the analytical technique was not adequate and must be corrected.

d. An action plan for evaluating and remediating data problems such as the high metal content in field blanks, sulfate duplicate data and poor precision within aluminum, iron and other metal data must be stated. Future sampling techniques are to be standardized in accordance with the Standard Operating Procedures (SOPs). This should eliminate the potential for variability due to sample volume.

19. Page 4-4, Section 4.3, Field QC Samples:

a. How are duplicate sediment samples taken? Normally, this is very difficult to do in the field. Please elaborate. The report indicates on page 4-5 that the sediment QC samples show non-detect field blanks and poor precision with respect to some metals. This may be a problem with the technique used in taking duplicate samples.

b. The text states that the sediment QC samples show poor precision with respect to selected metals. It then states that this implies that there is heterogeneity in the sediment being sampled or that variability arises from the sampling technique. The report should contain some discussion regarding this. Which is it? Why? How will the problem be corrected?

20. Page 4-9, third paragraph: This section of the report mentions that the 1990 program will include analysis of additional dissolved solids. Please provide specific information on exactly what analyses will be conducted and a rationale supporting the choices.

21. Page 5-3, first paragraph: The report states that a parametric ANOVA was performed for HCO_3 in groundwater. However, table 5-3 indicates that a non-parametric ANOVA was performed for this analyte. Please check the discrepancy and correct the text as needed.

22. Page 5-4, Section 5.2.2, Major Ion Geochemistry:

a. In the construction of trilinear diagrams, water quality data for the weathered sandstone and the weathered claystone were combined. This should not be done. Groundwater quality is likely to be quite different in the sandstone than in the claystone.

b. The report speculates that there may be a locally occurring sulfate source in the vicinity of wells B303089 and B201289. Include some discussion as to what the source may be.

c. Include plots showing changes in concentration with downgradient distance for colluvial wells and bedrock wells.

d. Provide an explanation of why the colluvium and valley fill would have higher TDS than that for the Rocky Flats Alluvium given that they are derived sediments from the Rocky Flats Alluvium.

e. The geochemical correlation of water systems for the surficial deposits and the weathered claystone and sandstone must be evaluated against the hydrogeology.

23. Page 5-16, Section 5.3.1, Statistics: The results for SW080 and SW104 indicated poor analytical and sampling techniques for part of the sampling rounds. The stations must be considered in the statistical evaluation. If poor results can be attributed to inadequate sampling and analytical methods, then the data can be removed from the analysis. Otherwise, the data must be included and statistically analyzed.

24. Page 5-18, Section 5.3.2, Major ion Geochemistry:

a. For the purpose of this background study, separate trilinear diagrams should be prepared for Woman Creek and Rock Creek. Until a temporal analysis is completed for the surface waters they should be analyzed separately.

b. Surface water characterization for Rock Creek is based, in part, on three surface water stations that are approximately a mile or more apart from each other. Conclusions regarding changes in water chemistry along Rock Creek can be misleading given the distance between the sampling stations. The uncertainty in any conclusions based on this data should be indicated in the text.

c. The stiff diagram for SW107 does not indicate elevated Na+K and Cl which is not consistent with the text. Please check and correct as required.

25. Page 5-22, Section 5.3.3, Surface Water Geochemistry:

a. EPA does not agree with the statement that total radioactivity/radionuclide concentrations are relevant to risk assessments. This is not true for certain pathways. For example, for the drinking water pathway, dissolved radioactivity data is more relevant. Also, it is incorrect to state that radionuclide standards are established for total, not dissolved concentrations. Typically, radionuclide standards are established for soluble or insoluble forms of the radionuclides. In either case, the standard that is being referenced must be described accurately.

b. An explanation for the selection of the set of metals used for figures 5-13 and 5-14 is necessary. A different set was used for each figure. Are these the only metals which follow the TSS pattern?

26. Page 5-23, second paragraph: At TSS concentrations reaching almost 30 gms/L, there is no question that the suspended material is contributing to the high concentrations of gross alpha radioactivity and radium 226. Clearly, sampling procedures must be improved.

27. Page 5-30, Section 5.5, Borehole Materials: Given the nature of formation of surficial deposits, it is reasonable to think of the Rocky Flats Alluvium as having a different borehole geochemistry than the bedrock units. It does not seem reasonable that the colluvium would be substantially different from the Rocky Flats alluvium and yet similar to the underlying bedrock units.

28. Page 5-33, Section 5.5.2, Tolerance Intervals: It is not correct to compute one set of statistics for borehole data for the combined group of colluvium, weathered sandstone, and weathered claystone. These lithologic units should not be grouped.

29. Table 5-14, Statistics for Dissolved Radiochemical Concentrations in Background Rocky Flats Alluvial Groundwater Samples: The upper tolerance limit calculation for U-238 appears to be restrictive. Background concentrations of U-238 which are several times higher than the reported value would not be unusual. For Pu-239 and Am-241 however, we expect the background concentrations to be less than the MDA's. The maximum concentration for Ra-226 (170 pCi/L) is unusually high for this area.

30. Table 5-19, Statistics for Dissolved Radiochemical Concentrations in Background Colluvial Groundwater Samples: The upper tolerance limit calculations for alpha, beta, and U-238 appear to be unrealistically high for background conditions. The use of unvalidated data, the problems with the blank subtracted

data, the limited number of data points, and/or problems with sampling techniques could all possibly contribute to this seemingly erroneous result. DOE must recognize the improbability of true background concentrations being this high with some discussion in the text of the report and should provide a plan for correcting the inherent problem in future reports. Other results that are questionable are indicated in the remaining comments.

31. Table 5-47, Statistics for Dissolved Radiochemical Concentrations in Background Upper Most Flow System Ground Water Samples: The upper tolerance limit calculations for alpha, beta, Ra-226, U-238, and U-235 appear to be unrealistically high for background conditions.

32. Table 5-56, Statistics for Total Radiochemical Concentrations in Background Surface Water Samples: The upper tolerance limit calculations for Am-241, Pu-239, alpha, beta, and Ra-226 appear to be unrealistically high. The same calculation for Ra-228 appears to be ridiculous.

33. Table 5-59, Statistics for Total Radiochemical Concentrations in Background Sediment Samples: Are the units for the sediment samples expressed as field weight or dry weight measurements? The upper tolerance limit calculations for Ra-228 and Sr-90 appear to be unrealistically high for background conditions.

34. Table 5-73, Statistics for Total Radiochemical Concentrations in Background Colluvial, Weathered Claystone, and Weathered Sandstone Borehole Samples: As is the case for bottom sediment samples, these units need to be defined as representing dry weight basis or field weight basis (excluding tritium). The upper tolerance limit calculation for Ra-228 appears to be unrealistically high. If this limit actually represents existing conditions, then thorium 232 analyses should be conducted.

35. Tolerance Interval Calculations for Total Radiochemical Concentrations in background Surface Water Samples: The results for gross alpha, Ra-226, and Ra-228 appear to be unrealistically high.

36. Tolerance Interval Calculations for Total Radiochemical Concentrations in Background Sediment Samples: The upper tolerance limit calculations for Ra-228 appear to be unrealistically high. Also, since we believe that the tritium results for sediment samples may represent the overlying water column, these two data sets should be similar. If negative results would not have been used in the statistical analysis, this comparison might have been achieved.